

Durability of flame-retardant finishes using a new phosphate-free laundry detergent

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Abstract: Flame-retardant finished fabrics normally lose their flame retardancy after relatively few home launderings using soap flakes or soap powder. This loss is attributed to the formation of lime soaps in and on the fabric. But when a sufficient amount of a phosphate-free lime soap-dispersing agent (LSDA) is incorporated in tallow soap-based detergents, the lime soap formation in and on the fabric is prevented or reduced and the fabrics can be laundered repeatedly without loss of flame retardancy.

THE EFFECT OF LAUNDERING VARIABLES on flame-retardant fabrics has received considerable scrutiny in the past decade. Chief among these variables is the selection of the cleaning agent, namely the soap or detergent. Recognition of the deleterious effects of soap powders or soap flakes was concurrent with the issuance on Oct. 1, 1964, of the British Home Office regulations governing the sale of children's night dresses. At that time garments made from flame-resistant fabrics, as well as the fabrics themselves when sold by the yard, were sold with a printed card giving washing instructions. The cards recommended by brand name eight nationally advertised (Great Britain) soapless detergents and warned against the use of soap powder or soap flakes. It was pointed out that the use of soap could leave flammable deposits, particularly when the wash water was hard.¹

A detailed study at the Southern Regional Research Center using soap and laundering in both moderately hard (approximately 100 ppm total hardness) and soft (10 ppm or lower) water showed the loss of flame retardancy caused by laundering with soap in moderately hard water.² This loss was attributed to the formation of calcium and magnesium "lime soaps." When these soaps were removed by acetic

acid extraction, flame retardancy was regained.

Recently,^{3,4} efficient soap-based heavy duty detergents were developed at the Eastern Regional Research Center of the US Department of Agriculture. Tallow soap was the major ingredient in these detergent formulations. Precipitation of calcium and magnesium soap in hard water was prevented by incorporating a lime soap-dispersing agent (LSDA). The mechanism of action of an LSDA has been explained by Stirton and coworkers.⁵ In the soap micelle in soft water, the soap molecules are oriented so that the hydrophilic $-COO^-$ portions of the molecules are facing outward. In the presence of Ca, Mg or other polyvalent ions in the water, the micelles invert exposing the hydrophobic long alkyl chains to the exterior of the micelle. This inversion results in precipitation of the familiar hard water scum.

An LSDA is a surfactant characterized by a bulky hydrophilic group or groups. When an LSDA is added to soap and the resulting mixture is dispersed in water, a mixed micelle is formed. Because of the hydrophilic bulk of the LSDA, the mixed micelle retains its curvature even in hard water, so that no inversion and precipitation occur. The soap-LSDA based formulations studied here proved excellent detergents in soft and hard water and caused no buildup of lime soap or redeposition of soil on the washed fabric.⁴

This preliminary study's purpose was to determine the effectiveness of these experimental tallow soap detergents in reducing the lime soap deposit and consequent loss of flame retardancy on suitably flame-retardant finished cotton fabrics.

Procedure

Four flame-retardant cotton fabrics were used in this study. The fabrics and

finishes were as follows:

(1.) A THPOH-ammonia oxidized retardant on 80 x 80 all-cotton printcloth. When tetrakis(hydroxymethyl)phosphonium chloride (THPC) is neutralized with an equivalent of sodium hydroxide per mole of THPC, the resulting product, for convenience, is referred to as "THPOH"; it has not been completely identified, but is known to consist mainly of tris(hydroxymethyl)phosphine and formaldehyde. When THPOH is exposed to ammonia, a highly insoluble polymer forms very rapidly.⁶ One outstanding feature of this finish is its effect on fabric strength: there is usually an increase, while most other finishes cause a reduction. Studies⁷ have shown that the oxidation of this polymer to the pentavalent state greatly improves the resistance of the flame retardant to sunlight.

(2.) A commercial phosphonate finished all-cotton flannelette which currently is marketed for use in children's sleepwear. The finish is based primarily on a cotton reactive product resulting from the reaction of a dialkyl phosphite and acrylamide^{8,9} with subsequent methylation with formaldehyde. The finish is normally applied together with a crosslinking agent such as trimethylolmelamine. The fabric is padded through a solution of the above, dried and then cured. This procedure is followed by an alkaline afterwash. Tensile strength losses are 20-30%.

(3.) THPOH-amide finished cotton sateen. When THPOH is applied in conjunction with urea and trimethylolmelamine and dried and then heat cured, flame retardancy is enhanced and there is less stiffness and strength loss (10 to 20% lower) than with the THPC-amide finish.¹⁰

(4.) THPC-amide finished cotton sateen. THPC is applied together with urea and trimethylolmelamine resins and an acid acceptor such as triethan-

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olamine. The treated fabric is dried, and then heat cured.^{11,12} Fabric so treated is somewhat stiffer and usually has a greater loss of tensile strength than similar fabrics-treated with the THPOH-amide finish.

Two LSDA tallow soap detergent formulations were used. The first part of the study was conducted using 120 g per washer load of an experimental detergent which was a dry blend of the following ingredients:

Tallow soap	80%
Sodium metasilicate	10%
Sodium methyl α -sulfotallowate (LSDA)	10%

The second wash study used a more sophisticated, spray dried, homogeneous formulation with increased silicate and LSDA. One hundred grams per washer load of the following formulation was used:

Ingredient	%
Tallow soap	64
Sodium silicate (1 Na ₂ O:1.6 SiO ₂)	15
Sodium methyl α -sulfotallowate (LSDA)	19
Sodium CMC	1.0
Optical brighteners	0.5
Impurities	0.5

The wash and tumble dry procedures were essentially those described in the American Association of Textile Chemists and Colorists Test Method 124-1969. The washing was done with New Orleans, La., city water having a total hardness of about 100. The vertical flame test used was that described in the American Association of Textile Chemists and Colorists Test Method 34-1969 using 12-sec flame exposure. A sample was considered to have failed if one or more specimens had a char length exceeding 6 in.

The phosphorus, calcium, and magnesium contents were determined by an X-ray fluorescent method using a General Electric* XRO-5 diffractometer modified for fluorescence analysis.¹³

Results

In the first series of washes using 120 g of the lower (10%) LSDA tallow detergent, all fabric samples failed the vertical flame test after 50 wash cycles. The elemental analyses of these samples are given in Table I along with that of an untreated cotton towel (UT) included in the wash cycles.

In the second wash series the higher LSDA content (about 19%) tallow deter-

gent was used. In this series only 100 g of the detergent was used in each wash. With the exception of the commercially finished fabric (Sample No. 2) all of the flame-retardant finished fabrics passed the vertical flame test after 50 wash cycles. Elemental analyses of the samples after 50 washes are given in Table II.

Table I
Flame-retardant cotton fabrics,
first wash series, elemental
analysis after 50 washes,
10% LSDA detergent

Sample No.	Ca	Mg	P
1	1.28	0.34	3.36
2	1.63	0.56	2.09
3	0.95	0.31	2.08
4	0.81	0.25	1.33
UT	1.10	0.25	0.14

Table II
Flame-retardant cotton fabrics,
second wash series, elemental
analysis after 50 washes,
19% LSDA detergent

Sample No.	Ca	Mg	P
1	0.34	0.01	3.00
2	0.88	0.12	2.19
3	0.48	0.03	1.99
4	0.35	0.03	1.45
UT	0.12	0.01	0.11

Discussion

Two factors appear to improve the soap-based detergent's effect upon flame retardant finishes. One is the intimate mixing that occurs when a slurry is made of the ingredients prior to spray drying. A mechanical dry mix is so unhomogeneous that the components dissolve at the different rates, so conceivably some of the soap might have been precipitated by the polyvalent ions in the wash water before the LSDA had completely dissolved.

The second factor is the level of LSDA in the formulation. In a formulation study³ it was determined that a 10% level was barely adequate for good detergency and that a 19% concentration of LSDA improved the detergent's washing characteristics. The improvement in retention of flame retardancy after washing with 19% LSDA detergent is obvious. While less of this detergent (100 g) was used than in the first series of washes (120 g), one failing and three passing samples are reported compared to the four failures noted in the first series. The increase in lime soap-dispersing ability is evidenced by the significant decrease in Ca and Mg content of the second set as compared to the first.

While the 19% detergent was effective with the 100 ppm hardness water used in these tests, studies with 200 to

300 ppm hard water, which is not uncommon in the US, have not been carried out. However, a parallel study¹⁴ reported that after 25 successive washes with the soap-based detergent there is no more buildup of Ca or Mg on the fabric than was obtained with a commercial phosphate-built detergent.

The flame retardancy failure of Sample No. 2 in the second wash set might be explained by the almost 1% Ca retention of this sample. Expressed as tallow soaps this would represent a pickup of about 10% of the combustible Ca tallowates.

Still another possibility exists. Recent, and as yet unreported, studies at the Southern Center indicate that under certain conditions of washing and drying, the flame-retardant resin used in finishing Sample No. 2 can and does exhibit ion exchange properties. This could, in whole or in part, account for the high Ca content.

These new and as yet experimental phosphate-free tallow soap-based detergents could, after much more extensive experimentation, offer a possible solution to the problem of a satisfactory cleansing medium for home laundering of flame-retardant garments. □ □ □

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